Cluster formation at metal surfaces under bombardment with SF$_m^+$ ($m = 1, \ldots, 5$) and Ar$^+$ projectiles

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Abstract

We investigate the formation of ionic and neutral clusters emitted from a polycrystalline indium surface under bombardment with SF$_m^+$ ($m = 1, \ldots, 5$) and Ar$^+$ projectile ions at 10 keV impact energy. Mass spectra of secondary ions and sputtered neutral particles are recorded under otherwise identical conditions. The neutral species are post-ionized prior to mass analysis by means of single photon-ionization using an intense UV laser at a wavelength of 193 nm. It is found that the measured secondary ion signals increase much more than those of the corresponding neutral particles if SF$_m^+$ projectiles are used instead of Ar$^+$ ions, indicating that the ionization probability under bombardment with SF$_m^+$ is enhanced by a chemical matrix effect induced by fluorine incorporation into the surface. Interestingly, the largest values of the ionization probability are observed for SF$_3^+$ projectiles. The total sputtering yield is found to be larger for SF$_m^+$ compared to Ar$^+$ projectiles and to increase linearly with increasing $m$. Both findings are shown to be understandable in the framework of linear cascade sputtering theory. The partial sputtering yields of In$_n$ clusters exhibit a stronger enhancement than the sputtered monomers, the magnitude of the effect increasing with increasing cluster size and projectile nuclearity.

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1. Introduction

When a solid is bombarded with energetic ions, particles are released from the surface due to a cascade of mostly elastic collisions (“sputtering”). It is well known that the sputtered flux contains agglomerates of several or many atoms (clusters), the formation of which still represents an intriguing phenomenon in sputtering physics [1]. So far, most experimental studies of sputtered clusters have been performed under bombardment with monoatomic – mostly rare gas – ions (cf. [1,2]).
The total sputtering yield under bombardment with polyatomic projectiles has been studied for more than three decades [3,4]. More recently, experimental data on the emission of secondary cluster ions under these conditions have been obtained. The results reveal that the use of such projectiles may significantly enhance the total sputtering yield [5,6] as well as the partial yields of secondary molecular and cluster ions [7–12]. One prominent example projectile that has been demonstrated to be very effective in secondary ion mass spectrometry (SIMS) of organic surfaces is SF$_5^+$. More specifically, it has been shown that particularly the signal measured for complex molecular secondary ions may be drastically enhanced under SF$_5^+$ bombardment as compared to rare gas or O$_2^+$ projectile ions [8,9,13–17]. A similar enhancement was observed if a Si(100) surface is bombarded with SF$_5^+$ and SF$^+$ ions in comparison to Xe$^+$ [18].

In most of these experiments, only the charged fraction of the sputtered flux (secondary ions) has been analyzed. Since it is known that the majority of sputtered particles generally leaves a metal surface as neutrals, it is not clear whether these observations reveal an enhancement of the partial sputtering yield of complex species or rather relate to an enhanced ionization probability, i.e. the probability that a sputtered particle becomes ionized in the course of the emission process. It is therefore necessary to perform similar experiments detecting the corresponding sputtered neutral species. Experimental data of this kind, however, are still scarce.

Self-sputtering a silver surface with Ag$_m^+$ cluster ions, Heinrich and Wucher [19,20] demonstrated an enhancement of neutral Ag$_n$ cluster yields upon transition from monoatomic to diatomic projectiles of the same impact velocity, a further transition to triatomic primary ions, however, resulted in an apparent reduction of the cluster formation efficiency. From our previous work [21], the secondary ion yields observed on a silver surface bombarded with SF$_5^+$ and Xe$^+$ under otherwise identical conditions exhibited a much more pronounced increase than the corresponding neutral yields, if SF$_5^+$ projectiles were used instead of Xe$^+$.

In the present work, we expand on these observations by systematically varying the nuclearity and fluorine content of the projectile. Indium is used as target material since (i) it is known that rare gas ion bombardment of an indium surface produces large amounts of In$_n$ clusters and (ii) the photoionization of sputtered neutral indium atoms and clusters is easily saturated using single photon-ionization at a convenient wavelength of 193 nm [22]. By comparing the secondary ion yields with those of the corresponding neutrals, it is possible to unravel the behavior of the partial sputtering yields and ionization probabilities as a function of the fluorine content and nuclearity of the projectile. Such information is needed in order to obtain a better understanding of the formation mechanisms of sputtered cluster ions under bombardment with chemically reactive polyatomic projectiles.

The results show that the ionization probability of sputtered In atoms and In$_n$ clusters is drastically enhanced under SF$_m^+$ bombardment as compared to Ar$^+$ bombardment. The magnitude of this enhancement depends on the projectile fluorine content and maximizes at $m = 3$. In comparison, the enhancement of the total sputtering yield is shown to be rather small.

2. Experimental

The experiments are performed in a laser post-ionization reflectron time-of-flight mass spectrometer described in detail elsewhere [23,24]. Briefly, a polycrystalline metallic indium sample is bombarded under 45° incidence with Ar$^+$ or SF$_m^+$ ($m = 1, \ldots, 5$) ions at 10 keV impact energy.

The ion beam is generated by a commercial cold cathode plasma ion source (Atomika Microfocus). The beam current drastically depends on the conditions of the ion generating plasma, which we know from our previous work to be unstable when the source is operated with pure SF$_6$ gas. In order to achieve enhanced stability and permit a rapid switching between different projectile ions, the ion gun is therefore operated with a gas mixture of 52% argon and 48% SF$_6$ and the desired projectiles are selected by means of a Wien filter. The
typical ion currents of different projectiles that are delivered under these conditions are displayed in Fig. 1.

During data acquisition, the primary ion beam is operated in a pulsed mode with a pulse duration of 10 μs at a repetition rate of 10 Hz. Neutral species which are sputtered from the indium surface are post-ionized by single photon absorption from an intense, pulsed UV laser beam operated at a wavelength of 193 nm, a pulse energy of 10 mJ and a pulse duration of about 20 ns. The ionizing beam is steered closely above and parallel to the sample surface with a cross-section of about 2.5 mm² in the interaction region located about 1 mm above the surface, the resulting peak power density being around 2 × 10⁷ W/cm². It was verified that under these conditions the photoionization efficiency is saturated, i.e. the measured signals of post-ionized neutrals are practically independent of the laser pulse energy or peak power density. This indicates that all neutral atoms and clusters present in the interaction volume – determined by the ion optical acceptance of the TOF spectrometer – are ionized with minimal fragmentation of the sputtered clusters.

Secondary ion spectra are measured by simply switching the ionization laser off and leaving the remainder of experiment unchanged. This way, secondary ions and neutrals are detected under otherwise identical experimental conditions [25]. The ionization probability is directly determined from the ratio between the secondary ion signals (measured without the ionizing laser) and the saturated secondary neutral signals without any further correction [26]. In all cases, the sample was sputter cleaned by dc ion bombardment prior to the acquisition of each mass spectrum.

3. Results and discussion

3.1. Neutral clusters

Mass spectra of post-ionized sputtered neutral atoms and clusters ejected from a polycrystalline indium surface under bombardment with 10-keV Ar⁺, SF⁺₅, SF⁺₄, SF⁺₃, SF⁺₂ and SF⁺ ions are illustrated in Fig. 2. Depending on the signal level, the different traces depicted in each panel were recorded with different detection methods (direct charge digitization or single ion pulse counting, respectively [24]). In addition, the signals of sputtered monomers and dimers were blanked from reaching the detector during acquisition of the pulse counting spectra of larger clusters in order to avoid detector saturation.

It is seen that sputtered neutral clusters containing up to 16 atoms can be identified under bombardment with SF⁺₅, SF⁺₄ and SF⁺₃, whereas Ar⁺, SF⁺₂ and SF⁺ projectiles allow the detection of clusters containing up to 12 atoms. While the mass spectrum obtained under Ar⁺ bombardment is relatively clean, small peaks corresponding to InₙF and InₙS clusters are observed under SF⁺ₙ bombardment. The formation of these molecules is caused by a projectile induced S and F contamination of the surface. The magnitude of the corresponding signals is almost negligible for sputtered neutrals but quite strong in the secondary ion spectra.

Note that the spectra obtained under SF⁺₅ and SF⁺₄ are almost identical. The integrated signals of sputtered neutral clusters – normalized to the primary ion current – are displayed as a function of the cluster size in Fig. 3. Since all other experimental parameters are identical, the resulting sig-

![Fig. 1. Projectile ion current delivered by the primary ion source operated with a mixture of Ar and SF₆ gas versus mass of different projectiles (Ar⁺ and SF⁺ₙ with n = 1, ..., 5).](image-url)
nal variation directly represents the variation of the respective partial sputtering yields under bombardment with different projectiles. It is apparent that the yields of neutral indium atoms and dimers sputtered from an indium surface under Ar\(^+\) bombardment are smaller compared to those produced under SF\(_m^+\) cluster ions by factors ranging from 1.8 to 2.7 for atoms and from 1.6 to 2.9 for dimers.

### 3.2. Secondary cluster ions

The integrated signals of secondary In\(^+\) ions and In\(_m^+\) cluster ions – normalized to the primary ion current – are shown in Fig. 4. As for the sputtered neutral particles, the difference between the curves directly represents the variation of the respective secondary ion yields induced by the different projectiles. The first important observation is that in all cases of SF\(_m^+\) projectile bombardment the yields of secondary ions are higher than those produced under Ar\(^+\) bombardment. A second important observation is that – upon transition from Ar\(^+\) to SF\(_m^+\) – the yield increase of secondary ions is much more pronounced than that of the corresponding neutral species. From Figs. 3 and 4, it is seen that the magnitude of the enhancement is small for sputtered atoms and dimers and increases with increasing sputtered cluster size.
3.3. Ionization probabilities

As described in Section 2, the ionization probabilities $\alpha_{X}^+ \times$ of sputtered particles $X$ are determined from the direct comparison of secondary ion and neutral signals via

$$\alpha_{X}^+ = \frac{S(X^+)}{S(X^0) + S(X^+)}.$$  \hspace{5cm} (1)

The resulting values for indium atoms and clusters generated by different projectiles are depicted in Fig. 5. It is seen that the ionization probability produced under $\text{Ar}^+$ bombardment is small compared to that observed under $\text{SF}_5^+$, $\text{SF}_4^+$ and $\text{SF}_3^+$ impact. Moreover, all ionization probabilities are small compared to unity, and the neutral yields are therefore directly representative of the respective partial sputtering yields.

Note that the largest enhancement of the ionization probability is observed for In atoms. For clusters, the enhancement is smaller and almost independent of the cluster size. We attribute this enhancement to a chemical matrix effect induced by the incorporation of fluorine from the projectile into the surface. In this context, it is interesting to note that the ionization probabilities exhibit an ordering according to $\alpha_{\text{In}}^+(\text{SF}_5^+) > \alpha_{\text{In}}^+(\text{SF}_4^+) > \alpha_{\text{In}}^+(\text{SF}_3^+)$. At first sight, this result is surprising because one would intuitively expect the highest ionization probability for the projectile containing the largest number of fluorine atoms ($\text{SF}_5^+$). More specifically, one would assume a monotonic depend-
ence on the surface concentration of fluorine, which must under sputter equilibrium conditions be determined by a balance between implantation and re-sputtering of F atoms described by

\[ c_F^S \propto \frac{m}{Y_{tot}(SF_m^+)} \]  

In Eq. (2), \( m \) is the nuclearity of fluorine in the projectile and \( Y_{tot} \) denotes the total sputtering yield.

The relative variation of \( Y_{tot} \) between different projectiles can be determined from the weighted sum of the primary ion current normalized neutral signals \( S(n) \) presented in Fig. 4 according to

\[ Y_{tot} \propto \sum_n n \cdot S(n). \]  

The resulting total sputtering yield as a function of the projectile size is shown in Fig. 6. In order to arrive at absolute values, the data have been normalized to a yield value of 10.4 atoms/ion which was calculated for 45°, 10-keV Ar+ impact using the SRIM2003 computer simulation package [27]. This was done since no experimental data on indium sputtering yields are available in the range around 10-keV impact energy either for Ar+ or SF\textsubscript{m}+ projectiles.

It is seen that the total sputtering yields are larger for SF\textsubscript{m}+ compared to Ar+ projectiles and increase linearly with increasing projectile fluorine nuclearity. Both findings may be qualitatively interpreted in terms of the fact that our experiments have been performed under identical total kinetic energy of the impinging projectiles. Upon impact, the cluster projectiles disintegrate, and the kinetic energy of each individual constituent atom is lower for larger projectile clusters. According to linear cascade theory [28], the sputtering yield should be roughly proportional to the energy \( F_D \) deposited close to the surface. In order to estimate the variation of this quantity for different projectiles, we calculate its depth distribution \( F_D(x) \) from the normalized vacancy distribution \( f_{vac}(E_0, x) \) calculated for every projectile constituent separately using the SRIM computer simulation code. Assuming a linear superposition of effects induced by each projectile constituent, the resulting value of \( F_D \) at the surface \( (x = 0) \) imposed by the impact of an SF\textsubscript{m}+ projectile is determined as

\[
F_D(x = 0) = m \cdot f_{vac}^F(E_0^F, x = 0) \cdot E_0^F + f_{vac}^S(E_0^S, x = 0) \cdot E_0^S,
\]

where \( E_0^F \) and \( E_0^S \) reflect the kinetic energy partition between F and S projectile constituents, respectively. In evaluating Eq. (4), the calculated distributions \( f_{vac}(x) \) were averaged over a surface layer of \( \Delta x = 2 \) Å. The resulting values of \( F_D \) calculated for 10-keV Ar+ and SF\textsubscript{m}+ projectiles impinging under 45° are depicted in Fig. 7. It is evident that all SF\textsubscript{m} clusters will deposit more energy at the surface than the Ar projectile. Moreover, a larger cluster will deposit more of its energy closer to the surface, thereby producing a higher sputtering yield. Both predictions are in good agreement with our experimental observations depicted in Fig. 6.

According to linear cascade theory, the deposited energy should be proportional to the projectile stopping power \( (dE/dx)|_{E_0} \). Since both quantities are determined in the SRIM simulation code, we can compare their projectile dependence as shown in Fig. 7. In order to calculate the effective stopping
power, the same summation procedure as outlined in Eq. (4) is employed. It is seen that for SF\textsuperscript{+}\textsubscript{\(m\)} projectiles the linear dependence on fluorine nuclearity \(m\) is observed in both cases. Interestingly, the proportionality constant,

\[ x = \frac{F_D(x = 0)}{(dE/dx)}_{E_0}, \]

appears to be smaller for Ar\textsuperscript{+} (1.0) than for SF\textsuperscript{+}\textsubscript{\(m\)} projectiles (1.3). According to theory, this quantity should increase with increasing mass ratio between target and projectile [28]. The fact that we observe higher \(x\) for SF\textsuperscript{+}\textsubscript{\(m\)} therefore provides a good indication that the stopping of an SF\textsuperscript{+}\textsubscript{\(m\)} projectile is equivalent to the sum of the stopping of its constituents. A similar finding has been reported for Au\textsubscript{\(n\)} projectiles implanted into various metal and semiconductor target materials [29].

The sputtering yield data depicted in Fig. 6 can now be used to estimate the fluorine uptake of the surface as a function of projectile fluorine nuclearity \(m\). After evaluating Eq. (2) for different values of \(m\), it is found that the maximum fluorine uptake should occur for SF\textsuperscript{+}\textsubscript{\(5\)}. As a consequence, we have to conclude that either the ionization probability does not strictly monotonously depend on the surface concentration of fluorine, or that other factors must also play a role in the formation of secondary ions at SF\textsuperscript{+}\textsubscript{\(m\)}-bombarded surfaces. In fact, a similar observation as made here has been reported by Reuter and coworkers [30–32] who demonstrated that an increase of the surface fluorine uptake by bleeding F\textsubscript{2} into the vacuum chamber does not necessarily enhance the secondary ion yields. Moreover, they found that the ionization probabilities of atoms sputtered from metallic targets under CF\textsubscript{3}\textsuperscript{+} bombardment were higher than or at least equal to those found for O\textsubscript{2}\textsuperscript{+} projectiles. When comparing our results with those obtained in [30,32], it is of interest to note that (i) the primary ion current delivered from the ion source was largest at CF\textsubscript{3}\textsuperscript{+} [30,32] and SF\textsubscript{5}\textsuperscript{+} (our case) and (ii) the highest ionization probabilities have been observed for CF\textsubscript{3}\textsuperscript{+} [30,32] and SF\textsubscript{5}\textsuperscript{+} (our case). We deduce from these results that the projectile XF\textsubscript{3}\textsuperscript{+} (X = C, S, . . .) must have some specialty that makes it the most abundant ion in the plasma on one hand and the most effective projectile for the production of secondary ions on the other hand.

3.4. Partial sputtering yields

In order to discuss the efficiency of different projectiles with respect to cluster production in sputtering, we first define relative partial sputtering yields of In\textsubscript{\(n\)} clusters as

\[ Y_{rel}(In_n) = \frac{Y_{In_n}}{Y_{In}}. \] (6)

The yield enhancement of a sputtered cluster containing \(n\) atoms as a function of the projectile fluorine nuclearity \(m\) is then described by an enhancement factor

\[ k_{1,m}(n) = \frac{Y_{rel}(SF_{m})}{Y_{rel}(SF_5)}. \] (7)

The resulting values are plotted as a function of the cluster size \(n\) in Fig. 8. For the set of SF\textsuperscript{+}\textsubscript{\(m\)} projectiles, it is seen that the enhancement observed with increasing \(m\) is the more pronounced the larger the sputtered cluster. The largest effect is found

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Fig. 7. Energy \(F_D\) deposited at the surface and effective projectile stopping power \((dE/dx)\) for impact of different 10-keV projectiles onto indium as a function of projectile mass. The data have been calculated using the SRIM2003 computer simulation package.
for In₉, the production of which is enhanced about 20 times as much as the total sputtering yield upon transition from SF⁺ to SF⁺₅ and Ar⁺ projectiles.

It should be noted that the increase observed for all sputtered clusters larger than dimers is non-additive in the sense that the value of $k_1$,m is larger than the atom ratio $(m + 1)/2$ between SF⁺₅ and SF⁺ projectiles. Since our work was performed under conditions of constant total impact energy rather than constant impact velocity, the values of k determined here cannot be directly compared to what has frequently been described as non-additive cluster yield enhancement measured for constant impact energy per constituent projectile atom [10,33–36]. In any case, the data presented in Fig. 8 provide clear evidence that the efficiency of cluster production is significantly increased during the progression from SF⁺ to SF⁺₅ projectiles. In principle, this finding is expected since it has been frequently observed that the relative abundance of sputtered clusters is correlated with the total sputtering yield [2]. More specifically, the cluster abundance distribution is changed in favor of large clusters with increasing total yield as long as atomic projectiles are used. For polyatomic projectiles, it has been demonstrated that this correlation may not be valid any more if the total yield significantly exceeds about 30 atoms/ion, indicating a transition into the “spike” regime of sputtering [19]. Since all sputter yield values determined here are below that limit, our data fit well into this picture.

Interestingly, the enhancement factors measured for Ar⁺ with respect to SF⁺ projectiles are practically identical to those determined for SF⁺₅. Hence, SF⁺₅ is not more efficient in producing sputtered clusters than Ar⁺, but more efficient than SF⁺₅ with smaller m. Particularly the former finding appears surprising, since the monoatomic Ar projectile penetrates deeper into the solid, leading to less deposition of energy immediately at the surface. As a consequence, the total sputtering yield imposed by Ar⁺ impact is smaller than those induced by SF⁺₅ projectiles (cf. Fig. 6), and one would therefore expect lower cluster abundances for Ar⁺. The fact that this is not observed may relate to the incorporation of projectile species into the surface. From statistical considerations, the yield of a sputtered Inₙ cluster should follow the indium surface concentration as $(c_{In})^n$. If $c_{In}$ is reduced due an S or F surface contamination, cluster formation will therefore be suppressed, the effect being the more pronounced the larger the sputtered cluster. The resulting yield reduction may in principle counterbalance the enhancement induced by the larger total sputtering yield. A quantitative estimate of the effect requires an in situ determination of the surface chemistry under SF⁺₅ bombardment which is outside the scope of the present study. Clearly, more data are needed to clarify that point.

4. Conclusion

The use of SF⁺₅ (m = 1, ..., 5) cluster ion projectiles to bombard an indium surface leads to a drastic increase of the ionization probability of sputtered In atoms and Inₙ clusters as compared to Ar⁺ ion bombardment at the same kinetic energy. This effect is attributed to a chemical matrix effect due to fluorine incorporation into the target surface. The largest value of the ionization probability is found for a projectile fluorine nuclearity of m = 3. This finding suggests that the formation of secondary ions cannot solely be determined by the fluorine surface concentration.
The total sputtering yield is found to be larger for SF$_m^+$ than for Ar$^+$ projectiles and to increase linearly with increasing $m$. Both findings are shown to be in agreement with the prediction of linear cascade theory. For SF$_m^+$ projectiles, the relative abundance of clusters in the total flux of sputtered particles is found to increase with increasing $m$, the enhancement being larger for larger sputtered clusters. This finding is in accordance with the general correlation between cluster abundance and total sputtering yield which has been found for many target materials under bombardment with monoatomic projectiles. From these observations, we conclude that non-linear effects do not play a dominant role for the system and impact energy studied here. No significant increase of relative cluster abundances, on the other hand, is found between Ar$^+$ and SF$_m^+$ projectiles, although the total sputtering yield induced by SF$_m^+$ projectiles is almost threefold larger than that induced by Ar$^+$. We suggest that this finding may be caused by the surface contamination under SF$_m^+$ bombardment which acts to suppress the formation of larger clusters.

It is obvious that detailed knowledge about the surface chemistry under reactive ion bombardment is needed in order to clarify the open questions with regard to both ionization probabilities and cluster abundance distributions measured under SF$_m^+$ ion bombardment. Corresponding experiments involving in situ photoelectron spectroscopy at the bombarded surface are currently under way in our lab.

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References


[27] Information on the SRIM program package can be found under http://www.srim.org.


